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● *Short Communication*

CRYSTALLIZATION OF POLY(ETHYLENE OXIDE) CONFINED IN PORES OF ACTIVE CARBON

A.V. FILIPPOV,* M.M. DOROGINIZKIJ,* AND R.SH. VARTAPETYAN†

*Department of Molecular Physics, Kazan State University, Kremlevskaya 18, Kazan; and †Institute of Physical Chemistry, Russian Academy of Sciences, Leninskii Prosp. 31, Moscow, Russia

The kinetics of isothermal crystallization of poly(ethylene oxide) confined in pores of active carbon was studied by nuclear magnetic resonance relaxation. At equal temperatures the induction period of crystallization in pores differs from that in the bulk polymer. A model was developed that allows estimation of the effect of porous media on the statistical sum of the macromolecule considering the change of the polymer chain conformation in the melt. This model describes the following observed effects: invariability of the induction period temperature dependence in pores, the weak temperature dependence of the ratio of induction period for e bulk, and pore material. The change in the induction period in cylindrical pores was predicted with satisfactory precision. © 1998 Elsevier Science Inc.

Keywords: **Nuclear magnetic resonance; Porous carbon; Poly(ethylene oxide); Polymer crystallization.**

INTRODUCTION

There is fundamental interest in the effect of the finite size constraints on physical properties of polymers confined in porous media, including crystallization. Basic principles of bulk polymer crystallization were described by Wunderlich.[1] Recently we studied the kinetics of the isothermal crystallization of poly(ethylene oxide) (PEO) in pores of active carbon.[2] It was found that isotherms of this process are similar in many ways to the majority of the polymer systems. For example, the S-type shape of the crystallization isotherms was observed, and the degree of the crystallinity attained as a result of the crystallization was less then 100%. At the same time for PEO confined in pores we found peculiarities that are not typical for PEO crystallization in the bulk. The degree of crystallinity attained decreased when the crystallization temperature (T_c) was increased. At the same time, the T_c induction period was longer, and the rate of the process was smaller for the polymer confined in pores. The isotherms of crystallization in Avrami plots was characterized by $n \sim 1$, compared to isotherms of the bulk crystallization described by $n \sim 2$. In this work we analyze the nature of the induction period change for polymers confined in pores.

The studied samples were PEO with M = 40000, $M_w/M_n \sim 1.1$ (Fluka-Buchs), and active carbon (ASG-100) with cylindrical pores. The mean pore diameter was estimated as ~480 Å from mercury porosimetry. Crystallization was studied directly in a nuclear magnetic resonance relaxometer probehead. The time of temperature equilibration in the sample was less than 1 min. The measured parameter was the dynamic degree of crystallinity, which was determined from the size of the transverse relaxation decay component with relaxation time ~10 μs, typical for the crystal phase of PEO. The induction period was determined as the time from the beginning of the process up to the moment when the first evidence of the crystallinity appears.

THEORY

Let ΔG_i be the free energy of a critical size nucleus formation. $\Delta G_i = \Delta H_i - T_c \Delta S_i$, where ΔH_i is the enthalpy of fusion, and $T_c \Delta S_i$ is the entropic term. Let us assume that the induction period, τ_i, is:

Address correspondence to Dr. A.V. Filippov, Department of Molecular Physics, Kazan State University, Kremlevskaya 18, 420008 Kazan, Russia